



The effect of cooling conditions on jet-cooked normal corn starch dispersions[☆]

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Abstract

When aqueous dispersions of normal corn starch are jet-cooked under excess steam conditions, the properties of the final product depend on the manner in which the cooked dispersion is cooled. Phase separation of amylose and amylopectin dramatically alters the final properties, and the extent of phase separation depends on the processing history of the sample. The aim of this study was to determine the effects of cooling rate, stirring rate and starch concentration on the rheology and microstructure of the cooled dispersion. A Rapid Visco Analyser was used to obtain a range of cooling profiles and stirring rates. Rheological measurements showed that samples that were stirred during cooling formed stronger gels than unstirred samples. Light microscopy revealed that after cooling, both irregular, amorphous particles and spherical or toroidal crystalline particles were observed in various proportions depending on starch concentration, cooling rate and stirring during cooling.

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1. Introduction

Steam jet cooking is a rapid and continuous process for preparing starch dispersions for industrial applications, for example, in the paper industry (Klem & Brogly, 1981). Under excess steam conditions, the high-temperature and high-shear conditions resulting from passing high-pressure steam through the hydroheater not only dissolves both the amylose and amylopectin components of the starch granule, but also reduces starch molecular weight (Byars, 2003; Dintzis & Fanta, 1996). Although the gelling and rheological properties of starch dispersions prepared by heating granular starch in water at atmospheric pressure have been studied extensively, the literature contains little information on starch dispersions prepared by steam jet cooking.

Research at our Center has focused on steam jet cooking as a method of combining starch with other materials to form new composite products. For example, Fanta, Shogren and Salch (1999) studied the role of fatty acid solubility in the formation of the helical inclusion complexes when high-amylose corn starch was jet-cooked with water-insoluble fatty acids as well as with their water-dispersible sodium salt forms. Only small differences were observed between the two cases, indicating that the high-temperature, high-shear conditions of the jet cooking process solubilized the fatty acids sufficiently to allow interaction with dissolved amylose.

When jet-cooked starch samples are allowed to cool slowly, crystalline particles can form. Davies, Miller and Proctor (1980) showed that the spherocrystals that formed from a cooked starch paste stored at 75–95 °C consisted of helical inclusion complexes of amylose with the native lipids present in the starch granule. They termed these crystallites high-temperature retrogradation products, since a high processing temperature in the jet cooker and a high storage temperature were required for their formation. Fanta, Felker and Shogren (2002) identified two types of

[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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crystalline particles that form when jet-cooked starches are cooled slowly. Normal corn starch, high amylose corn starch and rice starch each yielded small (5–15 μm diameter) toroidal particles, as well as larger (20–60 μm diameter) spherical particles. Waxy corn starch (which lacks amylose), defatted normal corn starch and potato starch (which lack lipids) did not form any crystallites upon cooling.

We are currently investigating starch–lipid composites prepared by jet cooking mixtures of starch and lipophilic materials, such as vegetable oils, that do not form helical inclusion complexes with amylose. In the course of this investigation, it was observed that low-shear stirring during cooling led to an increase in the final viscosities of these cooled, jet-cooked starch–oil dispersions (Eskins & Fanta, 1999). In this report, we expand upon this earlier work by using microscopy and rheological measurements of starch dispersions, prepared in the absence of added oil and cooled under controlled conditions, to understand how cooling and stirring conditions affect the microstructure and mechanical properties.

2. Materials and methods

2.1. Jet cooking

Normal corn starch (pure food-grade corn starch from A. E. Staley, Decatur, IL, USA) was suspended in distilled water using a Waring (East Windsor, NJ, USA) blender. The initial concentration of granular starch was varied from 7.0 to 14.1 wt% on an as is basis. This slurry was passed through a jet cooker under excess steam conditions, and the cooked starch was collected and analyzed. The slurry was delivered to the jet cooker by a Moyno progressing cavity pump (Robbins Meyers, Springfield, OH, USA) at a flowrate of about 1 l/min. The starch slurry and steam were combined in a Penick and Ford hydroheater (Penford Corp, Cedar Rapids, IA, USA). Steam was supplied at 580 kPa (70 psig), and the backpressure in the hydroheater was set at 380 kPa (40 psig). The cooked product was collected in a preheated Dewar flask. Percent starch solids in the jet-cooked dispersions was determined by freeze drying accurately weighed portions of each cooked dispersion. Determinations were carried out in replicate, and the results were averaged. The standard deviation of the solids concentration of the cooked dispersions was less than 0.2 wt% for each initial concentration.

For the experiments with defatted starch, samples were defatted by heating a stirred suspension of 175 g starch in 85 vol% methanol (1700 ml methanol plus 300 ml water) under reflux for 2 h (Morrison & Coventry, 1985). Starch was separated by filtration, and a second extraction was carried out under identical conditions. Two additional extractions were then carried out under the same conditions with refluxing 75 vol% *n*-propanol/water

(1500 ml *n*-propanol plus 500 ml water). The extracted starch was allowed to air dry and was further dried under vacuum at 55 °C.

2.2. Cooling conditions

A Rapid Visco Analyser (RVA) (Newport Scientific, Warriewood, NSW, Australia) was used to control the cooling rate and stirring conditions of the sample. Cooked starch (30 ml) was placed in a preheated sample cup and transferred to the RVA. All cooling profiles began with 2 min stirring at 360 rpm at 95 °C to eliminate any effects of sample handling and cooling during transport between the jet cooker and the RVA. Samples were cooled from 95 to 25 °C in either 4 h (~ 0.3 °C/min) or 1 h (~ 1.2 °C/min), with either stirring at 60 rpm or no stirring. In order to prevent drying of the sample during cooling, the top of the sample cup was sealed with an o-ring, so in this case the torque measurement of the RVA did not provide information about the viscosity of the sample during cooling.

2.3. Microscopy

Approximately 1 ml of sample was removed from the RVA cup and stored overnight at room temperature. Storage time did not affect the structure of samples as observed by microscopy. A drop of sample (30 μl) was placed on a glass slide, and a coverslip was applied and allowed to settle while the drop spread under the weight of the coverslip. After several minutes, the motion of the sample subsided and a stationary field was selected from near the middle of the sample to avoid areas subject to differential migration of particles. Samples were observed with a Zeiss Axioskop light microscope (Carl Zeiss, Inc., Thornwood, NY, USA) using phase contrast optics, and representative fields were photographed using a Kodak DCS 460 digital camera (Eastman Kodak Co., Rochester, NY, USA). The fields shown were chosen to display best the kinds of particles and domains contained in the sample, not necessarily reflecting their relative abundance.

2.4. Rheology

Measurements in small amplitude oscillatory shear flow were conducted on a Rheometrics (Piscataway, NJ, USA) ARES controlled strain fluids rheometer. Tests were performed with a 50 mm diameter cone-and-plate geometry. Small amplitude oscillatory shear measurements were conducted at a strain of 1%, which was within the linear viscoelastic region for all samples. A circulating water bath was used to maintain the temperature at 25.0 ± 0.1 °C, and humidity covers were used to prevent drying of the samples. All measures were performed in duplicate, and average values are reported. The standard deviations between repeated measurements for a given cooked dispersion, as well as between the average values

of measurements from multiple cooks cooled under the same conditions, were less than 10%.

3. Results and discussion

Results of the microscopy and rheology measurements are presented below to relate the microstructure of the sample to its mechanical properties, and to study how both are affected by cooling conditions. Phase contrast microscopy was chosen to examine microstructure to avoid artifacts due to dilution, staining or sample preparation. All measurements are for cooled samples that have attained steady values of their rheological properties, which were reached within two hours of the completion of the cooling.

In a previous study by Fanta et al. (2002), phase contrast microscopy revealed the formation of two classes of crystallites in slowly cooled jet-cooked starch dispersions: spherical crystallites approximately 10–30 μm in diameter, and more uniform, smaller, toroidal crystallites less than 10 μm in diameter. The size and structure of these particles were confirmed by scanning electron microscopy, and their crystallinity was established by both birefringence and X-ray diffraction. In this study, similar crystallites were recognized along with an abundance of a gel-like material with a mottled texture and containing irregularly shaped aggregates of indistinct particles of various sizes. This gel material was not observed in the prior study, which used more dilute starch dispersions (4.3 wt%).

Fig. 1a shows a light micrograph of a sample with a final solids content of 10.2 wt% that was cooled over four hours while being stirred. The image shows two large spherical crystallites ($\sim 20\text{--}30\ \mu\text{m}$ diameter) and a number of the smaller ($\sim 5\ \mu\text{m}$ diameter) toroidal crystallites previously described by Fanta et al. (2002). The majority of this image has a mottled texture containing rough, amorphous particles that appear to form a gel network in this sample. The interpretation of these areas as a gel network is based on the observation that before coming to rest under the cover glass, these domains move as blocks of material rather than independently, as do the spherical and toroidal crystallites. The grey background, visible in the lower left corner, for example, comprises the aqueous continuous phase. Fig. 1b shows the results of the linear viscoelastic measurements for the same sample as a function of frequency, ω . The storage modulus, G' , measures the elastic properties of the sample, while the loss modulus, G'' , measures its viscous properties. The response is typical of a weak gel, with G' nearly equal to G'' over most of the frequency range studied. Both moduli vary with frequency, although at the lowest frequencies, G' approaches a plateau.

The results in Fig. 2 are also for a 10.2 wt% starch dispersion cooled over four hours, but in this case the sample was not stirred during cooling. Both the spherical and toroidal crystallites are still formed under these conditions, but the particulate material indicative of gel

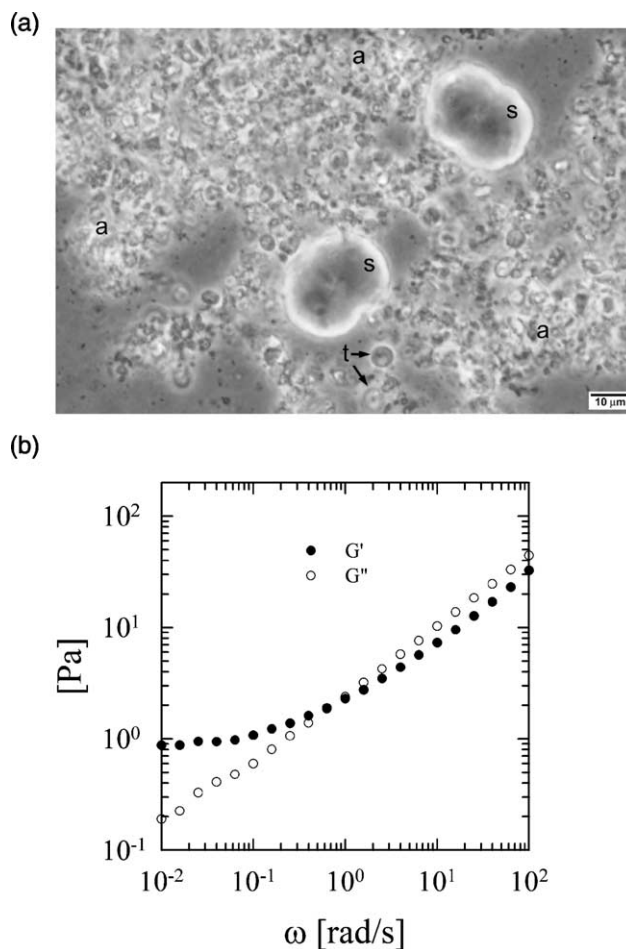


Fig. 1. (a) Phase contrast micrograph (a, amorphous gel network; s, spherical crystallite; t, toroidal crystallite) and (b) linear viscoelastic properties of a 10.2 wt% normal corn starch dispersion cooled in 4 h with stirring.

structure seen in Fig. 1a is absent (Fig. 2a). Irregular particles that are believed to be retrograded amylose are still present, but they are not associated to form a cohesive network as was the case for the stirred sample. The rheological measurements (Fig. 2b) show clearly the absence of gel behavior in the continuous phase, since $G' < G''$ at all frequencies, and both moduli increase with frequency over the entire measurement range. The effect of stirring on structure formation in these samples can be understood in terms of phase separation at high concentration between the amylose and amylopectin components of the starch dispersion. Without stirring, the two phases tend to separate (Doublier & Llamas, 1993; Kalichevsky & Ring, 1987). Amylose is therefore not available to interact with amylopectin to form a continuous amylose/amylopectin gel network. Instead, retrogradation and gelling take place in the aqueous amylose phase. Stirring inhibits this phase separation, and thus favors interaction and gel formation. There is evidence in the literature that interaction and gel formation (e.g. hydrogen bonding or entanglement) can occur between the two starch

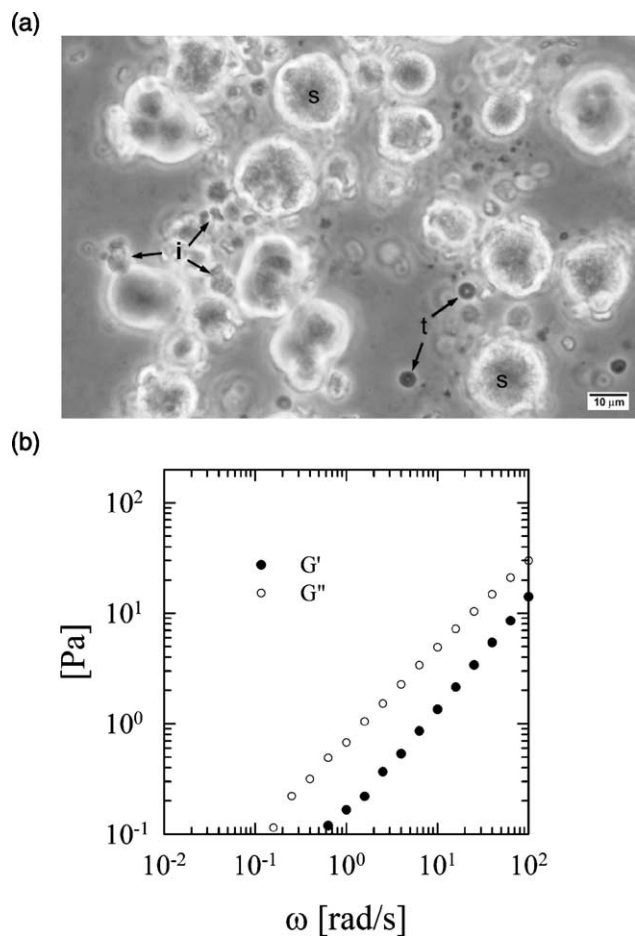


Fig. 2. (a) Phase contrast micrograph (i, irregular starch particles; s, spherical crystallite; t, toroidal crystallite) and (b) linear viscoelastic properties of a 10.2 wt% normal corn starch dispersion cooled in 4 h without stirring.

components (Jane & Chen, 1992; Klucinec & Thompson, 1999; Mestres, Colonna & Buleon, 1988; Rindlav-Westling, Stading & Gatenholm, 2002; Schierbaum et al., 1992; Tako & Hizukuri, 1999; Vorwerk, Schierbaum, Reuther & Kettlitz, 1988). No quantitative data are available on the effects of stirring on the selection of crystallite type, although both spherical and toroidal crystallites are formed in both cases shown here.

The importance of amylose in determining the gel properties was confirmed by experiments using waxy corn starch. At 10.2 wt%, the frequency dependence of the moduli for both stirred and unstirred samples was similar to that of the unstirred normal corn starch in Fig. 2b, although the values were a factor of two lower (data not shown). Furthermore, the modulus values of the stirred and unstirred samples of waxy corn starch were within 20% of each other over the entire frequency range. In contrast, the modulus values of the stirred normal corn starch sample in Fig. 1b were more than 10 times higher than the values for the unstirred sample in Fig. 2b at low frequencies.

Amylose and amylopectin do not phase separate as readily at lower concentrations, so stirring would not be

expected to change the nature of their interaction. This prediction is confirmed in Fig. 3a and b, which show micrographs for a 5.2 wt% dispersion cooled over four hours both with and without stirring. The most striking contrast with the higher concentration samples is the nature of the gel network. Fig. 3a and b show that the gel network has a much smoother texture, and it is similar for both stirred and unstirred conditions. The rheological measurements in Fig. 3c show that both samples form much stronger gels than at higher concentration, and here the unstirred sample is a slightly stronger gel. The values of the moduli

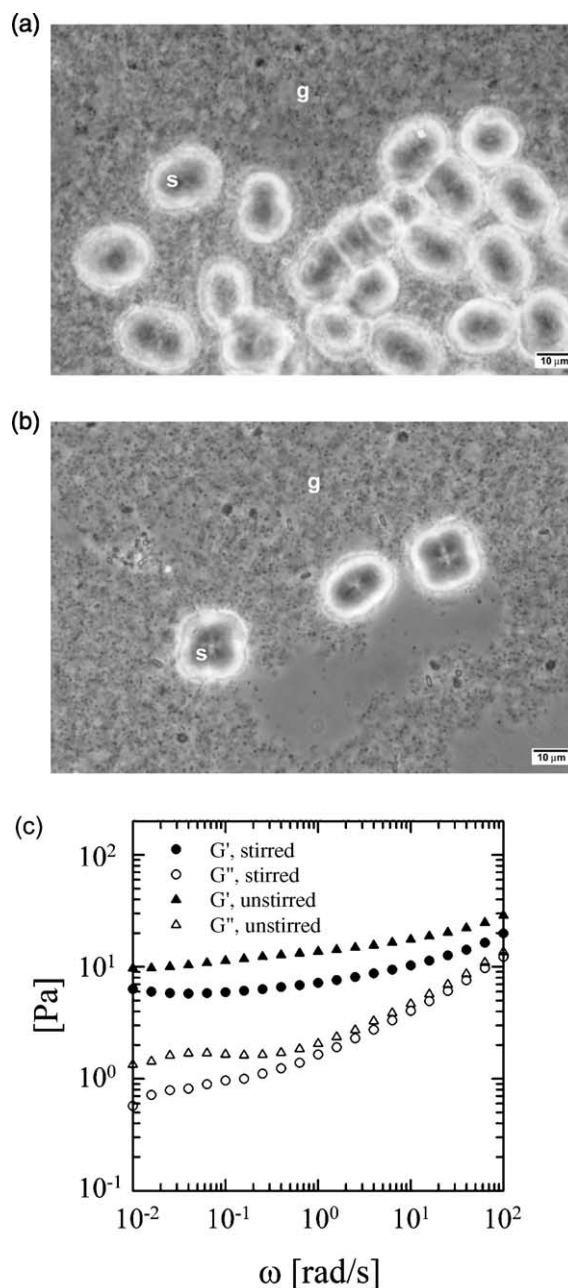


Fig. 3. (a, b) Phase contrast micrographs (s, spherical crystallite; g, gel network) and (c) linear viscoelastic properties of a 5.2 wt% normal corn starch dispersion cooled in 4 h with (a) and without (b) stirring.

are higher in this case than for the high concentration samples discussed above (Figs. 1b and 2b), and the qualitative features of the results are also characteristic of a strong gel, i.e. $G' > G''$ at all frequencies, and there is a much weaker frequency dependence of the moduli.

Experiments were also conducted with 5.2 wt% starch dispersions using defatted starch (data not shown). As expected for samples without native lipid, the crystallites were not observed, and the gel structure was similar to that of Fig. 3. The dynamic moduli showed a frequency dependence similar to that of the starch at 5.2 wt% that was not defatted, although their values were almost an order of higher magnitude. This suggests that sufficient amylose is complexed by native lipid, and is incorporated into crystallites, to have a significant effect on the rheology of the final product. Also, the presence or absence of native lipid can influence whether amylose or amylopectin forms the continuous phase in a phase-separated system (Doublier & Llamas, 1993). Formation of a continuous amylose phase, capable of forming a strong gel, is favored if amylose cannot interact with native lipid and then separate from solution as a water-insoluble complex.

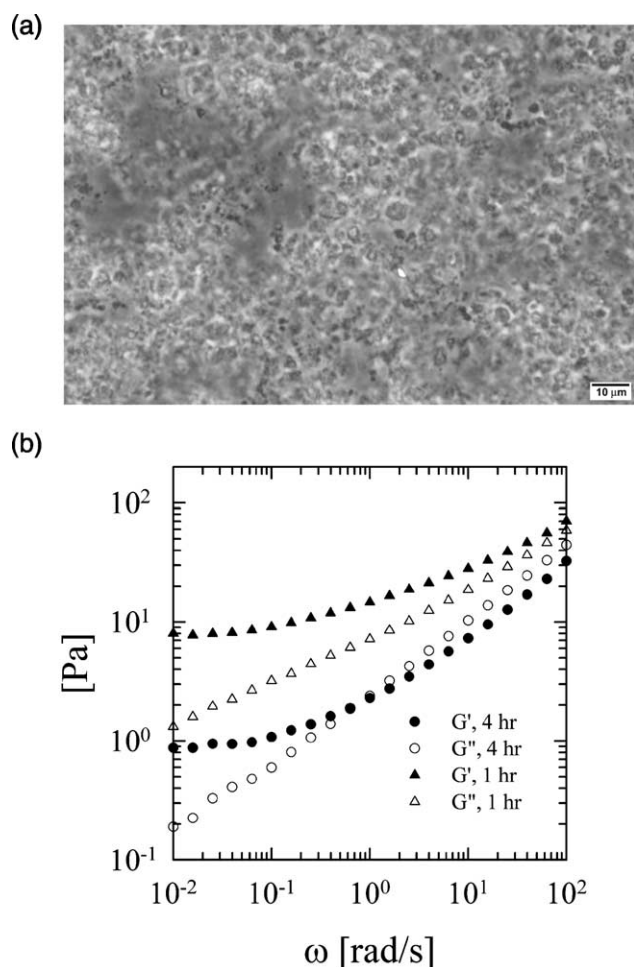


Fig. 4. (a) Phase contrast micrograph and (b) linear viscoelastic properties of a 10.2 wt% normal corn starch dispersion cooled in 1 h with stirring. The 4 h viscoelastic data is from Fig. 1b.

The effect of cooling rate on microstructure and gel properties is shown in Fig. 4, which shows results obtained with a 10.2 wt% starch sample that was cooled with stirring over a 1-h period, as opposed to the 4-h period shown in Fig. 1. The rough nature of the gel (Fig. 4a) is similar to the more slowly cooled sample, although in this case the spherical and toroidal crystallites are absent. This is consistent with the results of Davies et al., who found that an extended storage time above 75 °C was required for crystallite formation. The cooling time of 1 h produced a stronger gel than a 4-h cooling time (Fig. 4b), again suggesting that the amount of amylose that is complexed in the crystallites has a significant effect upon rheological properties. Detailed kinetic data on the rate of crystallite formation is not available, but Fig. 4 shows that a longer time than 1 h at elevated temperatures is required if the crystallites are to form. The faster cooling rate may also inhibit the phase separation of amylose and amylopectin, which would also lead to a stronger gel network.

The rheological results of an expanded series of experiments carried out with a 4-h cooling time are summarized in Fig. 5. The storage modulus (G') and loss modulus (G'') results are presented here in terms of

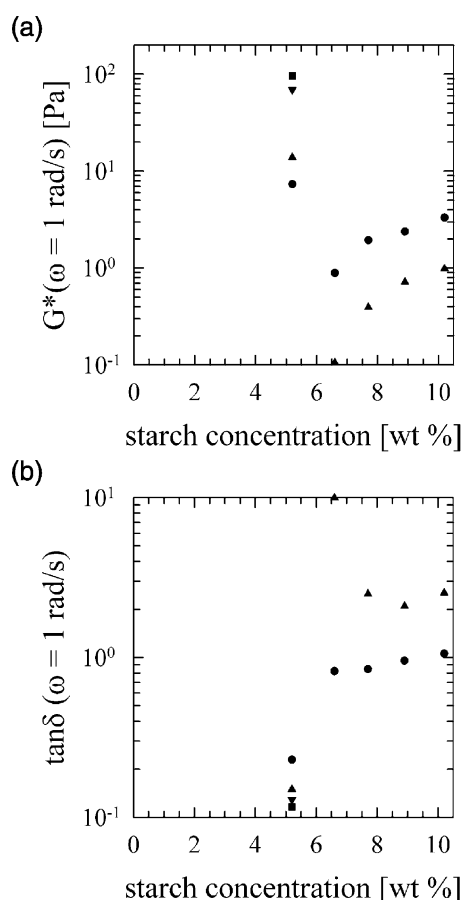


Fig. 5. (a) Complex modulus and (b) $\tan \delta$ for the normal corn starch samples cooled in 4 h. Results are shown for stirred (●), unstirred (▲), stirred (defatted) (▼) and unstirred (defatted) (■) samples.

the complex modulus and the loss tangent. A higher value of the complex modulus, $G^*(\omega) = [(G''(\omega))^2 + (G'(\omega))^2]^{0.5}$ (Fig. 5a), indicates a higher viscosity sample, and a lower value of the loss tangent, $\tan \delta = G''/G'$ (Fig. 5b) is characteristic of a stronger gel. All results in Fig. 5 were obtained at a frequency of 1 rad/s. Although the values of the moduli change with frequency, the same trends in concentration dependence of G^* and $\tan \delta$ were observed at other frequencies. At 5.2 wt%, amylose and amylopectin do not phase separate, and a stronger gel is formed, both in terms of the modulus values and $\tan \delta$. At 6.6 wt% and higher, phase separation is favored, and much weaker gels are formed than at lower concentrations. The effects of stirring are also much greater for the higher concentrations. Between 6.6 and 10.2 wt%, the complex modulus of the gel increased with starch concentration for both stirred and unstirred samples. Above 6.6 wt%, stirring resulted in nearly the same increase in complex modulus and decrease in loss tangent at each concentration.

4. Conclusions

The effects of cooling conditions on the microstructure and rheological properties of jet-cooked normal starch dispersions were studied. At high starch concentrations, the amylose and amylopectin components of the starch tend to phase separate. If a sample is stirred while being cooled, the phase separation is inhibited, leading to stronger gels. Stirring during cooling did not affect the formation of crystallites from helical inclusion complexes of amylose and fatty acids. However, for samples that were cooled more rapidly, the crystallites did not form, and a stronger gel was obtained. Below the critical concentration for phase separation, the amylose and amylopectin interact to form a stronger gel, and the properties of the final product are not significantly influenced by stirring. Experiments with a defatted starch produced a very strong gel with no crystallites. These results indicate the importance of processing history on the physical properties of jet-cooked starch dispersions.

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